



UNITED STATES PATENT AND TRADEMARK OFFICE

I, John Neil Albert SWEENEY BSc, PhD, Dip. Trans. IoL,
translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross,
Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the French and English languages.
3. That the attached is, to the best of my knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in France on 29 December 2000 under the number 00/17,310 and the official certificate attached hereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group plc
The 10th day of October 2001

INPI

INSTITUT
NATIONAL DE
LA PROPRIETE
INDUSTRIELLE

P A T E N T

UTILITY CERTIFICATE - CERTIFICATE OF ADDITION

OFFICIAL COPY

The Director-General of the Institut National de la Propriété Industrielle certifies that the attached document is a true copy of an application for industrial property titleright filed at the Institute.

Drawn up in Paris, 29 JUNE 2001

On behalf of the Director-General of the
Institut National de la Propriété Industrielle
The Divisional Head

(signature)

Martine PLANCHE

INSTITUT
NATIONAL DE
LA PROPRIETE
INDUSTRIELLE

REGISTERED OFFICE
26bis, rue de Saint Petersburg
75800 PARIS Cédex 08
Telephone: 33 (1) 53 04 53 04
Fax: 33 (1) 42 93 59 30
www.inpi.fr

INPIINSTITUT NATIONAL DE LA
PROPRIÉTÉ INDUSTRIELLE26 bis, rue de Saint Pétersbourg
75800 Paris Cedex 08
Telephone: 01 53 04 53 04
Telefax: 01 42 94 86 54**PATENT
UTILITY CERTIFICATE**

Intellectual Property Code - Book VI

REQUEST FOR GRANT 1/2

Cerfa

No. 11354*01

DB 540 W /190600

This form is to be filled in legibly in black ink

Reserved for the INPI		1. NAME AND ADDRESS OF THE APPLICANT OR THE REPRESENTATIVE TO WHOM THE CORRESPONDENCE IS TO BE ADDRESSED CABINET LA VOIX 2, Place d'Estienne d'Orves 75441 PARIS CEDEX 09 R 00172	
DATE OF SUBMISSION OF THE DOCUMENTS	29.12.00		
PLACE	75		
NATIONAL REGISTRATION No.	00/17,310		
GIVEN BY THE INPI			
DATE OF FILING GIVEN BY THE INPI		29 DEC. 2000	
Your file references: (optional) BFF 00/0656			
<input type="checkbox"/> No. given by the INPI to the fax			
2. NATURE OF THE APPLICATION		Tick one of the 4 following boxes	
Patent application		<input checked="" type="checkbox"/>	
Utility certificate application		<input type="checkbox"/>	
Divisional application		<input type="checkbox"/>	
Initial application		No. Date / /	
or initial utility certificate application		No. Date / /	
Conversion of a European patent application Initial application		<input type="checkbox"/>	
		No. Date / /	
3. TITLE OF THE INVENTION (200 characters or spaces maximum) Promoter of bismuth bisamide type.			
4. PRIORITY DECLARATION OR APPLICATION FOR THE BENEFIT OF THE FILING DATE OF A PRIOR FRENCH APPLICATION		Country or company	
		Date / / No.	
		Country or company	
		Date / / No.	
		Country or company	
		Date / / No.	
		<input type="checkbox"/> If there are other priorities, tick the box and use the "continuation" form	
		<input type="checkbox"/> If there are other applicants, tick the box and use the "continuation" form	
5. APPLICANT			
Name or company name		RHODIA CHIMIE	
Forenames			
Legal form		Société Anonyme	
SIREN No.			
APE-NF Code			
Street		26, Quai Alphonse Le Gallo 92512 BOULOGNE-BILLANCOURT CEDEX	
Address			
Postcode and town			
Country		FRANCE	
Nationality		French	
Telephone No. (optional)			
Fax No. (optional)			
E-mail (optional)			

REQUEST FOR GRANT 2/2

Reserved for the INPI		
DATE OF SUBMISSION OF THE DOCUMENTS	29 DEC. 2000	
PLACE	75 INPI PARIS	
NATIONAL REGISTRATION No.	00/17,310	
GIVEN BY THE INPI		
		DB 540 W /190600
Your file references: (optional)	BFF 00/0656	
6. REPRESENTATIVE		
Name		
Forename		
Firm or Company	CABINET LAVOIX	
No. of permanent power of attorney and/or contract		
Street	2 Place d'Estienne d'Orves	
Postcode and town	75441 PARIS CEDEX 09	
Telephone No. (optional)	01 53 20 14 20	
Fax No. (optional)	01 48 74 54 56	
E-mail (optional)	brevets@cabinet-lavoix.com	
7. INVENTOR (S)		
The inventors are the applicants	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no In this case, provide a separate designation	
8. SEARCH REPORT	For a patent application only (including division and conversion)	
Immediate compilation	<input checked="" type="checkbox"/>	
Deferred compilation	<input type="checkbox"/>	
Fee paid in instalments	Payment in three instalments, for natural persons only <input type="checkbox"/> yes <input type="checkbox"/> no	
9. REDUCTION OF THE RATE OF FEES	For natural persons only <input type="checkbox"/> Requested for the first time for this invention (attach [illegible]) <input type="checkbox"/> Requested prior to filing (attach copy of favourable decision for this invention or indicate its reference)	
If you used the "continuation" form, give the number of attached pages		
10. SIGNATURE OF THE APPLICANT OR REPRESENTATIVE (name and capacity of the signatory)	C. JACOBSON No. 92.1119 (signature)	SIGNED FOR THE PREFECTURE OR THE INPI [illegible signature]

Law no. 78-17 of 6 January 1978 relating to data processing, files and freedoms applies to the answers given in this form.
It guarantees right of access to and amendment of data concerning you held at the INPI.

INPIINSTITUT
NATIONAL DE
LA PROPRIÉTÉ
INDUSTRIELLE**PATENT****UTILITY CERTIFICATE**

Intellectual Property Code - Book VI

Cerfa

N° 11235*02

PATENTS DEPARTMENT

26 bis, rue de Saint-Petersbourg

75800 Paris Cédex 08

Tel: 01 53 04 53 04 Fax: 01 42 94 86 54

DESIGNATION OF THE INVENTOR(S) Page No. 1 / 2

(if the applicant is not the inventor or the sole inventor)

This form is to be filled in legibly in black ink

DB 113 W /260899

Your file references (optional)		BFF 00/0656	
NATIONAL REGISTRATION NO.		00/17,310	
TITLE OF THE INVENTION (200 characters or spaces maximum) Promoter of bismuth bisamide type.			
APPLICANT(S): RHODIA CHIMIE			
DESIGNATE(S) AS INVENTOR(S): (Indicate top right "Page 1/1". If there are more than 3 inventors, use an identical form and number each page, indicating the total number of pages.)			
Name		ROQUES	
Forenames		Nicolas	
Address	Street	37, rue Saint Nestor	
	Postcode and town		69008 LYON FRANCE
Employer company (optional)			
Name		DUBAC	
Forenames		Jacques	
Address	Street	2, chemin du Taur	
	Postcode and town		31320 PECHBUSQUE FRANCE
Employer company (optional)			
Name		LE ROUX	
Forenames		Christophe	
Address	Street	25, rue de Villegongis	
	Postcode and town		36000 CHATEAUROUX FRANCE
Employer company (optional)			
DATE AND SIGNATURE(S) OF THE APPLICANT(S) OR OF THE REPRESENTATIVE (Name and capacity of the signatory)		Paris, 15 May 2001 C. JACOBSON No. 92.1119 (signature)	

Law no. 78-17 of 6 January 1978 relating to data processing, files and freedoms applies to the answers given in this form.
It guarantees right of access to and amendment of data concerning you held at the INPI.

INPIINSTITUT
NATIONAL DE
LA PROPRIÉTÉ
INDUSTRIELLE**PATENT****UTILITY CERTIFICATE**

Intellectual Property Code - Book VI

Cerfa

N° 11235*02

PATENTS DEPARTMENT

26 bis, rue de Saint-Petersbourg

75800 Paris Cédex 08

Tel: 01 53 04 53 04 Fax: 01 42 94 86 54

DESIGNATION OF THE INVENTOR(S) Page No. 2 / 2

(if the applicant is not the inventor or the sole inventor)

This form is to be filled in legibly in black ink

DB 113 W /260899

Your file references (optional)		BFF 00/0656	
NATIONAL REGISTRATION NO.		00/17,310	
TITLE OF THE INVENTION (200 characters or spaces maximum) Promoter of bismuth bisamide type.			
APPLICANT(S): RHODIA CHIMIE			
DESIGNATE(S) AS INVENTOR(S): (Indicate top right "Page 1/1". If there are more than 3 inventors, use an identical form and number each page, indicating the total number of pages.)			
Name		REPICHET	
Forenames		Sigrid	
Address	Street	7, rue de la Fontanesque	
	Postcode and town	47500 MONSEMPRON-LIBOS	FRANCE
Employer company (optional)			
Name			
Forenames			
Address	Street		
	Postcode and town		
Employer company (optional)			
Name			
Forenames			
Address	Street		
	Postcode and town		
Employer company (optional)			
DATE AND SIGNATURE(S) OF THE APPLICANT(S) OR OF THE REPRESENTATIVE (Name and capacity of the signatory)		Paris, 15 May 2001 C. JACOBSON No. 92.1119 (signature)	

Law no. 78-17 of 6 January 1978 relating to data processing, files and freedoms applies to the answers given in this form.
It guarantees right of access to and amendment of data concerning you held at the INPI.



A subject matter of the present invention is novel bismuth amide derivatives, their application as Lewis acid, in particular for acylation reactions of aromatic compounds, and a corresponding preparation
5 process.

Acylation reactions of aromatic compounds, referred to as Friedel-Crafts type, represent a significant industrial commitment. Currently, AlCl_3 remains the most widely used promoter in industry for
10 this type of reaction. However, the need to use it in an at least stoichiometric amount has the major disadvantage of leading to significant production of waste (aluminum hydroxides and hydrochloric acid). There is consequently still an interest industrially in
15 novel catalysts which give better performances.

The present invention is targeted more particularly at providing the catalytic use of novel bismuth(III) salts.

BiCl_3 , a weak Lewis acid, has currently
20 already been provided for the acylation of activated aromatics. Its derivative, bismuth tris(triflate) ($\text{Bi}(\text{OTf})_3$), for its part exhibits an improved catalytic activity with respect to that of BiCl_3 and rare earth metal triflates. This is because it is capable of
25 carrying out the aroylation of unactivated or deactivated aromatic compounds.

The present invention is based more

specifically on the demonstration that it is advantageous to combine a ligand of Tf_2N^- type in a bismuth salt. This is because these bismuth salts display catalytic activities which are superior to those of their homologs of the triflate type. Thus it is that they prove to be effective in carrying out Friedel-Crafts benzylation and sulfonylation reactions. These two reactions are in fact known as being particularly difficult to carry out with conventional catalysts. Furthermore, with regard to industrial implementation, bismuth amide derivatives have the clear advantage of displaying an inertia with respect to standard solvents, in particular with respect to ethers, which is superior to that of the catalysts mentioned above, deriving in particular from aluminum.

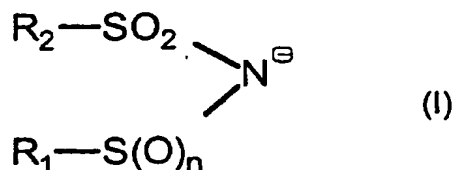
Consequently, a first subject matter of the present invention is a promoter of bismuth bisamide type.

The invention provides, in its second subject matter, the use of this type of promoter as Lewis acid catalyst and in particular as catalyst for carrying out benzylation and sulfonylation reactions of Friedel-Crafts type.

Finally, it provides a process of use in the preparation of the promoters in accordance with the present invention.

More specifically, a first subject matter of the invention is a promoter, characterized in that it comprises:

- at least one anion of formula (I):



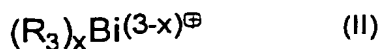
5

in which:

- R_2 represents a fluorine atom or advantageously an organic carbonaceous radical, if appropriate substituted by one or more halogen atoms and for which the carbon carrying the sulfonic functional group is perhalogenated, preferably perfluorinated, with R_1 and R_2 being able to be bonded to one another,
- n is equal to 1 or 2 with n preferably being equal to 2 when R_1 represents a fluorine atom,
- R_1 is an organic carbonaceous radical advantageously comprising at most 30 carbon atoms [when it is not polymeric (that is to say, does not constitute a bond for attachment to a polymer)] or a group as defined for R_2 , and

15

- at least one cation of formula (II):



with:

25

- x representing the integer 1 or 2, and

- the R_3 groups, which are identical or different, representing:

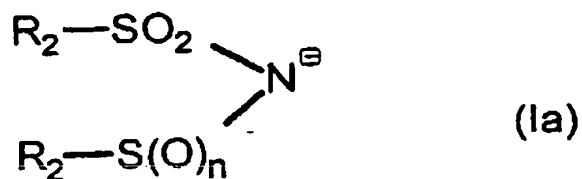
* a phenyl group, if appropriate substituted by one or more electron-donating substituents of linear or branched C_1 to C_4 alkyl type, such as, for example, methyl, ethyl or propyl, of C_1 to C_4 alkoxy type, such as methoxy, ethoxy, propoxy or phenoxy, or of C_1 to C_4 thioether type;

* a carboxylate group, such as acetate or sulfonate; or

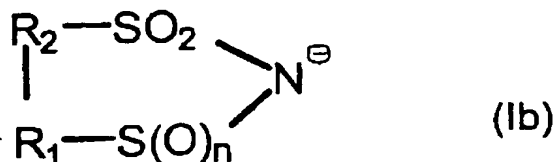
* a halogen atom, preferably chlorine, bromine and iodine;

with, when x is equal to 2, the two R_3 groups preferably being identical.

According to a preferred alternative form of the invention, the anion of formula (I) corresponds to the formula (Ia) or (Ib):



or



20

with, in the case of the formula (Ib), R_1 and R_2 having to represent a hydrocarbonaceous chain in

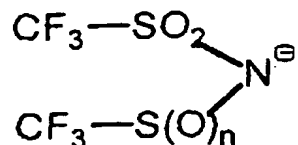
agreement with the definitions provided above for R_1 and R_2 .

According to a preferred form of the invention, the anion corresponds to the general formula (Ia) and R_2 is a fluorine atom or corresponds to the formula $\text{EWG}-(\text{CX}_2)_p-$, where:

- the X groups, which are alike or different, represent a fluorine atom or a radical of formula $\text{C}_{n'}\text{F}_{2n'+1}$ with n' being an integer at most equal to 5, preferably to 2, with the condition that at least one of the X groups is a fluorine atom,
- p represents an integer at most equal to 2,
- EWG represents an electron-withdrawing group, that is to say a group for which the sigma p is greater than 0, advantageously greater than 0.1 and preferably greater than 0.2, and for which the possible functional groups are inert under conditions of use of the promoter, advantageously a fluorine atom or a perfluorinated residue of formula $\text{C}_n\text{F}_{2n'+1}$ (Rf) with n' being an integer at most equal to 8, advantageously equal to 5, the total carbon number of Rf advantageously being between 1 and 15, preferably between 1 and 10.

According to a preferred form of the invention, the cation of formula (III) is represented by the formula $(\text{R}'_3)_x\text{Bi}^{(3-x)+}$ with R'_3 representing a phenyl group or a tolyl group.

As regards the anion of formula (I), it preferably corresponds to the formula:



with n representing 1 or 2 and preferably 2.

5 It is understood that the compounds of general formulae (I) and (II) are present in the said promoter in stoichiometric amounts sufficient to ensure the electrical neutrality of the promoter.

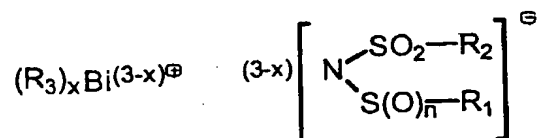
Thus it is that, in the case where x of the
10 formula (II) represents an integer equal to 1, one molecule of the corresponding compound of formula (II) is combined with two molecules of the compound of formula (I).

On the other hand, in the case where x has
15 the value 2, one molecule of the compound of formula (II), namely $(\text{R}_3)_2\text{Bi}^+$, is combined with one molecule of the compound of formula (I).

According to a preferred embodiment of the invention, x has the value 1.

20 As regards the combination between the two types of molecule, that is to say of formulae (I) and (II), it can be ionic or nonionic in nature.

Thus it is that the promoter can comprise the said compounds of general formulae (I) and (II) in the
25 form of a metal salt in the ionic state of type:



Although it is not intended within the meaning of the invention to be restricted to a specific chemical structure for the promoter, it is probable that, like the other bismuth(III) derivatives comprising electronegative atoms (Cl, OTf), the structure of the claimed promoter is a polymeric structure, the amide groups providing therein the bridges between the bismuth atoms. On this assumption, each bismuth atom is connected to 3 nitrogen atoms and to several oxygen atoms by $S=O \rightarrow Bi$ coordination. In fact, in the case of bismuth(III) triflate, which exists in several hydrated forms $(Bi(OTf)_3 \cdot nH_2O)$, with $n = 2, 4$ or 9 , it appears that the tetrahydrate is a dimer $[Bi(OTf)_3 \cdot 4H_2O]_2$ in which each bismuth atom is connected to 4 water molecules and three triflate groups, one of them providing a bridge with the other bismuth atom.

The promoters as defined above prove to be particularly effective as Lewis acids. The ligand of amide type probably induces, by its highly electron-withdrawing nature, a significant increase in the Lewis acidity at the bismuth atom with which it is combined. This therefore results in an increased catalytic activity of the said promoter.

Mention may more particularly be made, as

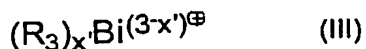
representatives of the promoters claimed as claimed in the invention, of $\text{BiPh}(\text{NTf}_2)_2$ and $\text{BiPh}_2(\text{NTf}_2)$.

A second aspect of the invention is targeted at the use of a promoter as defined as claimed in the
5 invention as Lewis acid.

The Lewis acidity of a reactant is the property defined quantitatively by measuring the equilibrium constant for formation of the Lewis adduct with a base taken as reference. Without being committed
10 to a specific mechanism, it seems that the bismuth will use the three 6p electrons to form three bonds, thus giving its more stable oxidation state (+3), while the two 6s electrons will be involved in the higher oxidation state (+5). Like the other heavy elements,
15 the presence of vacant 6d orbitals will then be responsible for the Lewis acidity of the bismuth(III) derivatives, that is to say for their ability to complex Lewis bases, such as carbonyl or sulfonyl groups.

20 The claimed promoters thus prove to be particularly efficient in catalysing such reactions as Diels-Alder reactions, carbonyl allylations, ene reactions and Prins reactions.

A subject matter of the present invention is
25 also more particularly the use of a promoter comprising at least one anion of formula (I) as defined above and one cation of formula (III):



with:

- R_3 being as defined above; and
- x' representing 0 or an integer having the value 1 or 2 with, in the case where x' is equal to 2, the R_3 groups being able to be identical or different, as catalyst of Lewis acid type for acylation, such as benzylation, and sulfonylation reactions of Friedel-Crafts type.

As emerges from the examples below, the catalyst corresponding to the definition according to the invention make it possible to efficiently carry out this type of reaction, which is known to be particularly difficult.

Furthermore, it has been noticed that the promoters comprising a derivative of formula $(R_3)Bi^{++}$ as cation have a reactivity virtually equivalent to that displayed by a promoter comprising the Bi^{+++} cation as counteranion of the compound of general formula (I).

This equivalence in terms of reactivity is particularly advantageous industrially insofar as the anions of general formula (I) are fairly expensive compounds.

The promoters $Bi(NTf_2)_3$, $BiPh_2(NTf_2)$ and $BiPh(NTf_2)_2$ prove to be particularly advantageous for the claimed use.

The promoters are generally introduced directly into the reactions to be catalysed.

These reactions are generally carried out in solvents such as aromatic hydrocarbons, for example toluene and benzene, and haloalkanes. Of course, these solvents must remain inert under the reaction
5 conditions.

Thus it is that, with $\text{Bi}(\text{NTf}_2)_3$, satisfactory yields of *o*-, *m*- and *p*-methylbenzophenone are obtained by acylation of toluene.

Of course, the promoter is used as Lewis acid
10 catalyst in an amount sufficient to initiate the expected reaction.

Without limiting the invention, the promoter can be employed in a proportion of 0.5 mol% to 100 mol%, expressed with respect to the substrate to be
15 converted.

It is more preferably present in a proportion of 5 to 20% and more particularly in a proportion of approximately 10%.

The invention applies more particularly to
20 the functionalization of optionally substituted aromatic compounds having at least one of the following rings:

- . a monocyclic or polycyclic aromatic carbocycle,
- 25 . a monocyclic or polycyclic aromatic hetero-cycle comprising at least one of the heteroatoms O, N and S.

It will be specified, without, however, limiting the scope of the invention, that this optionally substituted aromatic compound can represent:

1° - a monocyclic or polycyclic aromatic
5 carbocyclic compound.

The term "polycyclic carbocyclic compound" is understood to mean:

. a compound composed of at least 2 aromatic carbocycles forming, between them, ortho- or ortho- and
10 peri-condensed systems,

. a compound composed of at least 2 carbocycles, only one of which is aromatic, forming, between them, ortho- or ortho- and peri-condensed systems.

2° - a monocyclic or polycyclic aromatic
15 heterocyclic compound.

The term "polycyclic heterocyclic compound" defines:

. a compound composed of at least 2 heterocycles comprising at least one heteroatom in each ring,
20 at least one of the two rings of which is aromatic, forming, between them, ortho- or ortho- and peri-condensed systems,

. a compound composed of at least one hydrocarbonaceous ring and at least one heterocycle, at
25 least one of the rings of which is aromatic, forming, between them, ortho- or ortho- and peri-condensed systems.

3 - of a compound composed of a sequence of rings, as defined in paragraphs 1 and/or 2, bonded to one another:

- . by a valency bond,
- 5 . by an alkylene or alkylidene radical having from 1 to 4 carbon atoms, preferably a methylene or isopropylidene radical,

. by one of the following groups:

-O-, -CO-, -COO-, -OCOO-

-S-, -SO-, -SO₂-,

-N-, -CO-N-,

R ₀	R ₀

- 10 in these formulae, R₀ represents a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, a cyclohexyl radical or a phenyl radical.

Mention may be made, as examples of rings under 1° to 3°, of:

- 15 1° - benzene, toluene, xylene, naphthalene or anthracene,

2° - furan, pyrrole, thiophene, isoxazole, furazan, isothiazole, imidazole, pyrazole, pyridine, pyridazine, pyrimidine, quinoline, naphthyridine,

- 20 benzofuran or indole,

3° - biphenyl, 1,1'-methylenebiphenyl, 1,1'-isopropylidenebiphenyl, 1,1'-oxybiphenyl or 1,1'-iminobiphenyl.

In the process of the invention, a benzene compound is preferably employed.

The aromatic compound can carry one or more substituents. Mention may in particular be made, as
5 representatives of these substituents, of

- . an OH group,
- . a linear or branched alkyl radical having
from 1 to 6 carbon atoms,
- . a linear or branched alkenyl radical having
10 from 2 to 6 carbon atoms,
- . a linear or branched alkoxy radical having
from 1 to 6 carbon atoms,
- . a -CHO group,
- . an acyl group having from 2 to 6 carbon
15 atoms,
- . a -COOR₂ group where R₂ has the meaning
given above,
- . an -NO₂ group,
- . an -NH₂ group,
- 20 . a halogen atom, preferably a fluorine,
chlorine or bromine atom, and
- . a -CF₃ group.

Mention may more particularly be made, as illustration of these aromatic compounds, of:

- 25 - halogenated or nonhalogenated aromatic
compounds, such as benzene, toluene, chlorobenzene,
dichlorobenzenes, trichlorobenzenes, fluorobenzene,

difluorobenzenes, chlorofluorobenzenes, chlorotoluenes,
fluorotoluenes, bromobenzene, dibromobenzenes, bromo-
fluorobenzenes, bromochlorobenzenes, trifluoromethyl-
benzene, trifluoromethoxybenzene, trichloromethyl-
5 benzene, trichloromethoxybenzene or trifluoromethyl-
thiobenzene,

- aromatic amino or nitro compounds, such as
aniline and nitrobenzene,

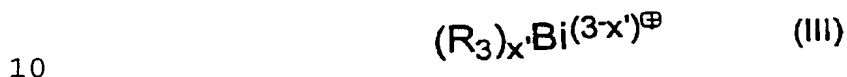
- phenolic compounds, such as phenol,
10 o-cresol or guaiacol,
- monoethers, such as anisole, ethoxybenzene
(phenetole), butoxybenzene, isobutoxybenzene, 2-chloro-
anisole, 3-chloroanisole, 2-bromoanisole, 3-bromo-
anisole, 2-methylanisole, 3-methylanisole, 2-ethyl-
15 anisole, 3-ethylanisole, 2-isopropylanisole, 3-iso-
propylanisole, 2-propylanisole, 3-propylanisole,
2-allylanisole, 2-butylanisole, 3-butylanisole, 2-tert-
butylanisole, 3-tert-butylanisole, 2-benzylanisole,
2-cyclohexylanisole, 1-bromo-2-ethoxybenzene, 1-bromo-
20 3-ethoxybenzene, 1-chloro-2-ethoxybenzene, 1-chloro-
3-ethoxybenzene, 1-ethoxy-2-ethylbenzene, 1-ethoxy-
3-ethylbenzene, 2,3-dimethylanisole or 2,5-dimethyl-
anisole,

- diethers, such as veratrole, 1,3-dimethoxy-
25 benzene, 1,2-diethoxybenzene, 1,3-diethoxybenzene,
1,2-dipropoxybenzene, 1,3-dipropoxybenzene,
1,2-methylenedioxybenzene or 1,2-ethylenedioxybenzene,

- triethers, such as 1,2,3-trimethoxybenzene, 1,3,5-trimethoxybenzene or 1,3,5-triethoxybenzene.

A third aspect of the invention relates to a process for preparing a promoter in accordance with the invention.

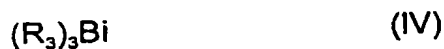
More specifically, it relates to a process for the preparation of a promoter comprising at least one anion of formula (I) as defined above and one cation of formula (III):



with:

- R_3 being as defined above; and
 - x' representing 0 or an integer having the value 1 or 2 with, in the case where x' is equal to 2, the R_3 groups being able to be identical or different, characterized in that:

• at least one compound of formula (IV):



with R_3 representing

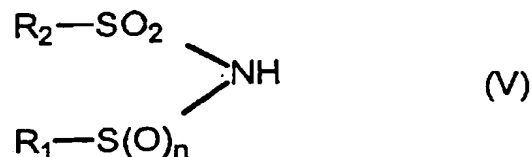
- a phenyl group, if appropriate substituted by one or more electron-donating substituents of linear or branched C_1 to C_4 alkyl type, such as, for example, methyl, ethyl or propyl, of C_1 to C_4 alkoxy type, such as methoxy, ethoxy, propoxy or phenoxy, or of C_1 to C_4 thioether type;

- a carboxylate group, such as acetate or sulfonate; or

- a halogen atom, preferably chlorine,
bromine and iodine;

with the R_3 groups being able to be identical
or different and preferably being identical,

5 is reacted with at least one compound of
formula (V):



with R_1 , R_2 and n being as defined above, and
in that said promoter is recovered.

10 Of course, the stoichiometry between the two
components is adjusted as claimed in the desired degree
of deprotometallation.

If it is desired to carry out a monodeproto-
metallation of the compound of general formula (IV),
15 the compound of general formula (V) is used in a
proportion of at most one equivalent.

On the other hand, if it is desired to carry
out at least two deprotometallation reactions on the
compound of general formula (IV), an excess of compound
20 of general formula (V) is employed.

Furthermore, in the specific case where it is
desired to successively carry out three deproto-
metallation reactions on the compound of general
formula (IV), it is advantageous to choose the R_3 groups
25 so as to enhance the electron density at the bismuth

atom.

This is because the fact that two groups of general formula (I) have already been fixed to the bismuth atom strongly deactivates the final R_3 group present on this same atom. Consequently, the presence of an electron-rich ligand bonded to the bismuth atom makes it possible to overcome this effect induced by the two groups of general formula (I) and helps in carrying out the final deprotometallation reaction. In this specific case, the R_3 groups present on the bismuth atom are thus preferably chosen so as to confer, on the latter, a charge at least equivalent to that conferred by three tolyl groups. More preferably, the three R_3 substituents are identical and represent a tolyl group.

The syntheses of the promoters are generally carried out in a solvent of haloalkane type, such as dichloromethane or dichloroethane, or a solvent of acetonitrile type, or toluene, and under an inert atmosphere. The bismuth salt is added gradually to the compound of general formula (V), dissolved beforehand in the cooled solvent.

The expected promoter is subsequently isolated.

The examples which appear below are presented by way of illustration and without implied limitation of the subject matter of the present invention.

EQUIPMENT AND METHOD

The GC analyses were carried out on a Hewlett-Packard GC 6890 chromatograph (BPX5 capillary column, 25 m \times 0.22 mm, 5% phenylpolysiloxane film).

5 The progress of the reactions is monitored using tetradecane as internal standard.

The GC-MS is a Hewlett-Packard unit composed of the 5890® chromatograph and the 5989® mass spectrometer.

10 The measurements are made on Bruker AC 80, 300 and 400 MHz spectrometers. The chemical shifts are expressed in the δ unit (ppm) with respect to TMS for ^1H and ^{13}C NMR and with respect to trifluoroacetic acid for ^{19}F NMR. The coupling constants are expressed in Hz. The
15 solvent used is d_6 -acetone.

IR spectrometry was carried out on a Perkin-Elmer model 1760-X spectrometer (5 000-400 cm^{-1}) using a cell with an AgCl plate.

The solvents used (toluene, dichloromethane)
20 are dried as claimed in the usual methods. Benzoyl chloride, toluoyl chloride, benzenesulfonyl chloride and benzoic anhydride are commercially available products. Bis(trifluoromethanesulfonyl)amide (Tf_2NH) was supplied by Rhodia Organique Fine. It is stored and
25 handled in a glove box. Silver bis(trifluoromethanesulfonyl)amide (AgNTf_2) was prepared as claimed in the method described in the literature [Vij A, Zheng YY,

Kirchmeier RL, Shreeve J, *Inorg. Chem.*, (1994) 33, 3281], along with tris (*p*-tolyl)bismuth [Gilman H, Yale HL, *J. Chem. Soc.*, (1941) 281].

EXAMPLE 1:

5 BiPh₂(NTf₂)

Tf₂NH (0.281 g, 1 mmol) is introduced into 10 ml of distilled CH₂Cl₂ in a 100 ml Schlenck flask purged with argon. The Schlenck flask is cooled to 0°C. A solution of BiPh₃ (0.44 g, 1 mmol) in 10 ml of CH₂Cl₂ 10 is added with a syringe. The mixture assumes an orange yellow colour and a compound which is insoluble in dichloromethane appears. The Schlenck flask is brought back to [lacuna] temperature and stirring is maintained for three hours. All the dichloromethane is evaporated 15 and the residue is dried under vacuum. A white BiPh₂(NTf₂) powder is obtained (0.60 g, 0.94 mmol), Yd 94%).

Spectroscopic characteristics of BiPh₂(NTf₂)

¹H NMR (400.13 MHz): δ: 7.50 (para, 1H, H_x, tt, J(H_xH_m) = 20 7.5 Hz, J(H_xH_a) = 1.2 Hz), 7.89 (meta, 2H, H_m, dd, J(H_mH_x) = 7.5 Hz, J(H_mH_a) = 7.8 Hz), 8.52 (ortho, 2H, H_a, dd, J(H_aH_m) = 7.8 Hz, J(H_aH_x) = 1.2 Hz).

¹⁹F NMR (376.48 MHz): singlet at δ = -1.79 ppm.

¹³C NMR (100.62 MHz): δ: 121.0 (q, J = 321 Hz, CF₃), 131.3 25 (s, CH), 133.7 (s, CH), 186.6 (s, CH), ipso C_q of the aromatic ring not displayed by NMR.

EXAMPLE 2:BiPh(NTf₂)₂

This involves the same process as that described for BiPh₂(NTf₂) starting from 2 mmol of Tf₂NH
 5 and 1 mmol of BiPh₃. A white BiPh(NTf₂)₂ powder is obtained (0.76 g, 0.9 mmol, 90%).

Spectroscopic characteristics of BiPh(NTf₂)₂:

¹H NMR (400.13 MHz): δ: 7.60 (para, 1H, H_x, tt, J(H_xH_m) =
 7.5 Hz, J(H_xH_a) = 1.2 Hz), 8.32 (meta, 2H, H_m, dd,
 10 J(H_mH_x) = 7.5 Hz, J(H_mH_a) = 8.3 Hz), 9.21 (ortho, 2H, H_a,
 dd, J(H_aH_m) = 8.3 Hz, J(H_aH_x) = 1.2 Hz).

¹⁹F NMR (75.393 MHz): singlet at δ = -2.1 ppm.

¹³C NMR (75.469 MHz): δ: 120.5 (q, J = 321 Hz, CF₃), 130.7
 (s, CH), 135.1 (s, CH), 138.8 (s, CH), ipso C_q of the
 15 aromatic ring not displayed by NMR.

EXAMPLE 3:Bi(NTf₂)₃:

A solution of Tf₂NH (0.85 g, 3 mmol) in 10 ml
 of CH₂Cl₂ is introduced under argon into a 100 ml
 20 Schlenck flask. The Schlenck flask is cooled in an ice
 bath and a solution of Bi(Tolyl)₃ (0.48 g, 1 mmol) in
 10 ml of CH₂Cl₂ is added with a syringe. The mixture
 instantaneously assumes an orange yellow colour and an
 insoluble compound appears. After stirring overnight at
 25 ambient temperature, the solvents are evaporated under
 vacuum. 1.01 g of a pale yellow Bi(NTf₂)₃ powder are
 thus recovered, i.e. a yield of 96%. This product is

stored and handled in a glove box.

Spectroscopic characteristics of Bi(NTf₂)₃:

¹H NMR (300.13 MHz): Absence of peaks.

¹⁹F NMR (376.47 MHz): singlet at $\delta = -1.77$ ppm.

5 ¹³C NMR (75.469 MHz): δ : 120.4 (q, J = 321 Hz, CF₃).

IR (CCl₄) ν (cm⁻¹): 1451 (very strong), 1305 (shoulder), 1231 (very strong), 1132 (very strong), 894 (shoulder), 855 (very strong), 650 (strong), 608 (very strong), 573 (shoulder), 502 (very strong).

10 EXAMPLE 4:

Catalytic benzoylation of toluene

All the handling is carried out under argon.

Toluene (4.6 g, 50 mmol), tetradecane (0.496 g,

2.5 mmol) and 5 mmol of the chosen acylating agent

15 (benzoic anhydride or benzoyl chloride) are successively introduced into a 50 ml two-necked flask equipped with a reflux condenser which already contains Bi(NTf₂)₃

(0.525 g, 500 μ mol). The stirred reaction mixture is placed in an oil bath at 110°C. The progress of the

20 reaction is monitored by GC by withdrawing, with a syringe, a small portion of the reaction mixture in order to determine the change in the yield of methylbenzophenone (*ortho*, *meta* and *para*). This analysis is complemented by a comparison of the chromatogram and
25 of the mass spectra (GC/MS) obtained on pure samples of *o*-, *m*- and *p*-methylbenzophenone [Aldrich; 15,753-8, 19,805-6, M2,955-9].

Percentage of ortho/meta/para isomers: 16/4/80
(from benzoyl chloride), 20/4/76 (from benzoic
anhydride).

- GC: Analytical condition: Starting temperature =
5 125°C
Final temperature =
300°C
Slope = 20°C/min

Retention time: *ortho*: 6.1 min; *meta*: 6.4 min;
10 *para*: 6.6 min.

- GC/MS [m/z(%)]:
o-methylbenzophenone: 196 (M⁺,60), 195(100),
119(24), 105(55), 91(41), 77(89).
p-methylbenzophenone: 196 (M⁺,57), 181(12),
15 119(100), 105(43), 91(41), 77(61).

EXAMPLE 5:

Catalytic sulfonylation of toluene

This involves the same process as that
described for the benzoylation. This analysis is also
20 complemented by a comparison of the chromatogram and of
the mass spectra (GC/MS) obtained on pure samples of o-,
m- and p-methyldiphenyl sulfone.

- GC: Analytical condition: Starting temperature =
125°C
25 Final temperature =
300°C
Slope = 20°C/min

Retention time: *ortho*: 7.8 min; *meta*: 7.9 min;
para: 8.1 min.

Percentage of *ortho*/*meta*/*para* isomers: 34/6/60
(starting from benzenesulfonyl chloride).

5 - GC/MS [m/z(%)]:

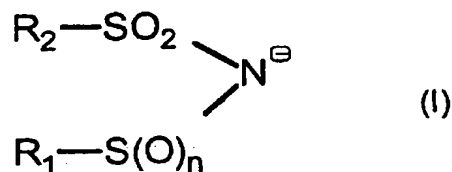
o-methyldiphenyl sulfone: 232 (M^+ ,25), 214(45),
166(72), 137(33), 91(35), 77(100).

p-methyldiphenyl sulfone: 232 (M^+ ,65), 139(75),
125(52), 107(67), 91(48), 77(100).

CLAIMS

1. A promoter, characterized in that it comprises:

- 5 • at least one anion of formula (I):

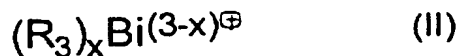


in which:

- R₂ represents a fluorine atom or an organic carbonaceous radical, if appropriate substituted by one or more halogen atoms and for which the carbon carrying the sulfonic functional group is perhalogenated, with R₁ and R₂ being able to be bonded to one another,

- n is equal to 1 or 2,
- R₁ is an organic carbonaceous radical or a group as defined for R₂, and

- 15 • at least one cation of formula (II):



with:

- x representing the integer 1 or 2, and
- the R₃ groups, which are identical or different, representing:

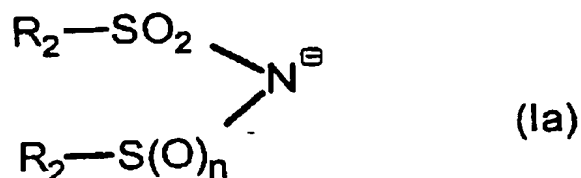
- * a phenyl group, if appropriate substituted by one or more electron-donating substituents of linear or branched C₁ to C₄ alkyl type, of C₁ to C₄ alkoxy type or of C₁ to C₄ thioether type;

* a carboxylate group; or

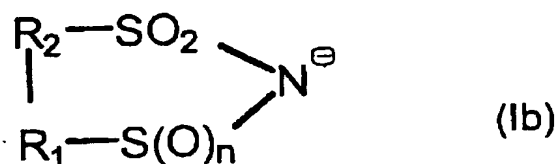
* a halogen atom.

2. The promoter as claimed in claim 1, characterized in that the anion of formula (I)

5 corresponds to the formula (Ia) or (Ib):



or



10 in which formulae R_1 , R_2 and n are as defined in claim 1.

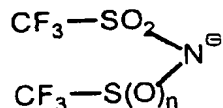
3. The promoter as claimed in claim 1 or 2, characterized in that the anion corresponds to the general formula (Ia) with R_2 representing a fluorine atom or corresponding to the formula $\text{EWG}-(\text{CX}_2)_p-$ in
15 which:

- the X groups, which are alike or different, represent a fluorine atom or a radical of formula $\text{C}_{n'}\text{F}_{2n'+1}$ with n' being an integer at most equal to 5, with the condition that at least one of the X groups is
20 a fluorine atom,

- p represents an integer at most equal to 2,
- EWG represents an electron-withdrawing

group, for which the sigma p is greater than 0,
preferably chosen from a fluorine atom or a
perfluorinated residue of formula $C_{n''}F_{2n''+1}$ (Rf) with n''
being an integer at most equal to 8, the total carbon
5 number of Rf being between 1 and 15.

4. The promoter as claimed in one of the
preceding claims, characterized in that the anion
corresponds to the formula:



10 with n representing 1 or 2.

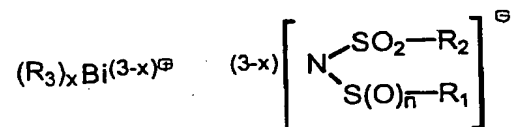
5. The promoter as claimed in one of the
preceding claims, characterized in that the cation is
represented by the formula $(\text{R}'_3)_x\text{Bi}^{(3-x)+}$ with R'_3
representing a phenyl group or a tolyl group.

15 6. The promoter as claimed in one of the
preceding claims, characterized in that it combines one
molecule of a compound of formula (II) in which x is
equal to 1 with two molecules of the compound of
formula (I).

20 7. The promoter as claimed in one of claims
1 to 5, characterized in that it combines one molecule
of the compound of formula (II) in which x has the
value 2 with one molecule of the compound of formula
(I).

25 8. The promoter as claimed in one of the
preceding claims, characterized in that it is provided

in the form of a metal salt in the ionic state of formula:

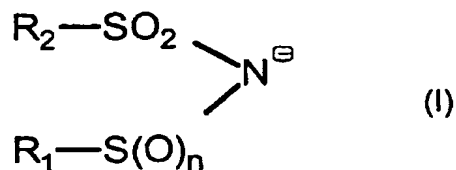


with R_3 , x , n , R_1 and R_2 being as defined in
5 claims 1 to 5.

9. The promoter as claimed in one of the preceding claims, characterized in that it is chosen from $BiPh(NTf_2)_2$ and $BiPh_2(NTf_2)$.

10. The use of the promoter as defined in
10 claims 1 to 9 as Lewis acid.

11. The use of a promoter comprising at least one anion of formula (I)



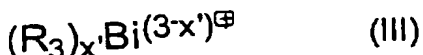
in which:

15 - R_2 represents a fluorine atom or an organic carbonaceous radical, if appropriate substituted by one or more halogen atoms and for which the carbon carrying the sulfonic functional group is perhalogenated, with R_1 and R_2 being able to be bonded to one another,

20 - n is equal to 1 or 2,

- R_1 is an organic carbonaceous radical advantageously comprising at most 30 carbon atoms or a group as defined for R_2 ,

and one cation of formula (III):



with:

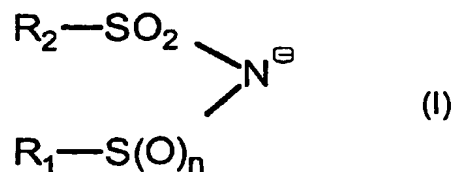
- R_3 being as defined in claim 1; and
- x' representing 0 or an integer having the value 1 or 2 with, in the case where x' is equal to 2, the R_3 groups being able to be identical or different, as catalyst of Lewis acid type for acylation and sulfonylation reactions of Friedel-Crafts type.

12. The use as claimed in claim 11, characterized in that the anion of formula (I) is as defined in claims 2 to 4.

13. The use as claimed in claim 11 or 12, characterized in that the promoter is chosen from $BiPh_2(NTf_2)$, $BiPh(NTf_2)_2$ and $Bi(NTf_2)_3$.

14. The use as claimed in one of claims 11 to 13, characterized in that the promoter is employed in a proportion of 0.5 mol% to 100 mol%, expressed with respect to the substrate to be converted.

15. A process for the preparation of a promoter comprising at least one anion of formula (I):



in which:

- R_2 represents a fluorine atom or an organic carbonaceous radical, if appropriate substituted by one or more halogen atoms and for which the carbon carrying

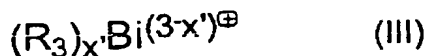
the sulfonic functional group is perhalogenated, with R_1 and R_2 being able to be bonded to one another,

- n is equal to 1 or 2,

- R_1 is an organic carbonaceous radical

5 advantageously comprising at most 30 carbon atoms or a group as defined for R_2 ,

and one cation of formula (III):



with:

10 - the R_3 groups, which are identical or different, representing:

* a phenyl group, if appropriate substituted by one or more electron-donating substituents of linear or branched C_1 to C_4 alkyl type, of C_1 to C_4 alkoxy type,
15 or of C_1 to C_4 thioether type;

* a carboxylate group; or

* a halogen atom;

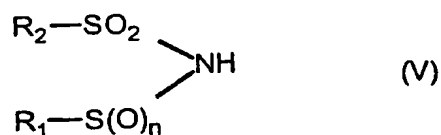
- x' representing 0 or an integer having the value 1 or 2 with, in the case where x' is equal to 2,
20 the R_3 groups being able to be identical or different, characterized in that:

• at least one compound of formula (IV):



with R_3 as defined above,

25 is reacted with at least one compound of formula (V):



with R_1 , R_2 and n being as defined above, and in that said promoter is recovered.

16. The process as claimed in claim 15, characterized in that at most one equivalent of compound of general formula (V) is employed per one compound of general formula (IV).

17. The process as claimed in claim 15, characterized in that an excess of compound of general formula (V) is employed with respect to the compound of general formula (IV).

18. The process as claimed in one of claims 15 to 17, characterized in that the compound of general formula (IV) has, as R_3 substituent, radicals which make it possible to obtain, at the bismuth atom, an electron charge at least equivalent to that conferred by three tolyl groups.

19. The process as claimed in one of claims 15 to 18, characterized in that the reaction is carried out under an inert atmosphere.

20. The process as claimed in one of claims 15 to 19, characterized in that the compound of formula (IV) is added gradually to the compound of formula (V).